

THE USE OF AN ALIPHATIC-AROMATIC DIACYL PEROXIDE IN A **BLEACHING COMPOSITION**

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Technical field

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The present invention relates to the use of an aliphatic-aromatic diacyl peroxide in a bleaching composition.

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Background

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Peroxygen bleach-containing compositions typically based on hydrogen peroxide have been extensively described in laundry applications as laundry detergents, laundry additives or laundry pretreaters.

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An example of such a bleaching agent is a diacyl peroxide. Diacyl peroxides and compositions containing such compounds, including dialiphatic, diaromatic and aliphatic-aromatic diacyl peroxides have been described in the prior art.

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JP1009601 (KAO) describes a composition comprising hydrogen peroxide, a diacyl peroxide and a surfactant. The diacyl peroxide can be dialiphatic, diaromatic or aliphatic-aromatic. The composition is described to have good storage stability.

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WO98/11189 (Procter & Gamble) describes a process for bleaching a fabric with a liquid composition comprising a dialiphatic peroxide. This document does not describe aliphatic-aromatic diacyl peroxides.

It has been found that although diaromatic peroxides provide good stain removal, they are aggressive bleaching agents that cause fabric damage, resulting in poor fabric colour safety.

It is believed that a radical decomposition of hydrogen peroxide occurs on the surface of the fabric, generating free radicals. It is further speculated that this generation of free radicals may provide an aggressive decomposition of certain dyes present in the fabrics, resulting in chemical damage of dye molecules visible as discoloration and/or loss of colour intensity. Thus, bleaching performance and fabric colour safety are somewhat conflicting requirements, but both are desirable in a single bleaching composition.

It is therefore an objective of the present invention to provide a bleaching composition that provides good stain removal and good fabric colour safety.

European patent number EP-A-742 279 and EP-A-752 469 disclose laundry bleaching compositions containing chelating agents, radical scavengers and polyamines, and which are safe to colors and fabrics. The peroxygen bleaches disclosed therein include peroxy acids such as diperoxydodecandioic acid but do no describe aliphatic-aromatic diacyl peroxides.

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It has now been found that the above objectives can be met by using an aliphatic-aromatic diacyl peroxide to treat soiled fabrics. Indeed, it has been found that the mixed aliphatic-aromatic diacyl peroxide, especially in an aqueous bleaching composition, delivers good stain removal performance on fabrics, when compared to the use of the same composition either without an aliphatic-aromatic diacyl peroxide or comprising a dialiphatic diacyl peroxide. Also, it has been found that the mixed aliphatic-aromatic diacyl peroxide, especially in an aqueous bleaching composition, reduces the colour damage of colored fabrics (i.e. improves colour safety), when compared to the colour damage observed with the same composition but comprising a different peroxygen bleach, for

example a diaromatic diacyl peroxide, instead of said aliphatic-aromatic diacyl peroxide.

An advantage of the present invention is that the improved stain removal performance obtained is consumer noticeable on a variety of stains/soils, including enzymatic stains like blood, grass, and especially carotenoid-type stains like tomato sauce.

Thus, the applicant has found that the diacyl peroxides of the present invention provide not only good stain removal but also provide good fabric colour safety.

Summary of the invention

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According to the present invention there is provided the use of a diacyl peroxide having the general formula:

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wherein R1, is an aliphatic group and R2 is an aromatic group to provide stain removal and improved fabric colour safety.

Detailed description of the invention

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Diacyl peroxide

The diacyl peroxide of the present invention has general formula:

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wherein R1 is an aliphatic group and R2 is an aromatic group. In a preferred aspect of the present invention R1 has from 1 to 30, more preferably 4 to 20 carbon atoms. R1 may be linear, branched, cyclic, saturated, unsaturated, substituted, unsubstituted or mixtures thereof. Preferably R1 is linear and comprises from 8 to 16 carbon atoms. Where R1 is substituted, the carbon atom is preferably substituted with a halide or sulpate-containing or nitrogen-conatining functionality such as SO3-, SO4-, NO2, NR3+ where R = H or alkyl chain.

R2 may be mono or polycyclic aromatic ring, homo or heteroatomic aromatic ring, substituted or unsubstituted and mixtures thereof. Where R2 is substituted, the carbon atom is preferably substituted with a halide, sulphur-containing functionality, nitrogen-containing or an alkyl chain wherein the number of carbon atoms ranges from 1 to 20, most preferably from 4 to 10. Suitable sulphur-containing or nitrogen-containing substituents include SO3-, SO4-, NO2, NR3+ where R=H or an alkyl chain. Preferably R2 is benzene. In a preferred embodiment of the present invention the diacyl peroxide is preferably benzoyl alkanoyl peroxide wherein the alkanoyl group has from 8 to 18 carbon atoms. More preferably the diacyl peroxide is selected from the group consisting of benzoyl lauroyl peroxide, benzoyl decanoyl peroxide, para-alkyl benzoyl lauroyl peroxide, para-alkyl benzoyl cetoyl peroxide, para-alkyl benzoyl cetoyl peroxide and mixtures thereof. In a particularly preferred embodiment the diacyl peroxide is benzoyl lauroyl peroxide.

The diacyl peroxides described herein are easily synthesized by persons skilled in the art, see for example Organic Peroxides Vol. 1; page 65, edited by Daniel Swern of Wiley Interscience.

The present invention also relates to the use of a bleaching composition comprising the diacyl peroxides described herein. Where the present invention relates to a bleaching composition, the diacyl peroxide is typically present in the range of from 0.01% to 10% preferably 0.1% to 3%, more preferably from 0.3% to 2% and most preferably from 0.5% to 1% by weight of the composition.

The compositions used according to the present invention may further comprise another peroxygen bleach in addition to said aliphatic diacyl peroxide, hereinafter called the "second" peroxygen bleach. Additional optional ingredients may be added in said compositions, for example bleach activators, surfactants, brighteners, chelating agents, radical scavengers, stabilisers, soil suspending polymers, soil release agents, dye transfer inhibiting agents, solvents, colourants, rheology modifiers, sud suppressors catalysts, perfumes, or mixtures thereof. Preferred optional ingredients are described in more detail hereinafter.

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In a preferred embodiment of the present invention, it has been found that the use of preferably aqueous bleaching compositions comprising a diacyl peroxide as describe herein, and a second peroxygen bleach, provide improved stain removal performance and bleaching performance whilst still ensuring good fabric colour safety, as compared to the same compositions but without said diacyl peroxide described herein. Thus, the present invention also encompasses the use of a bleaching composition preferably comprising from 0.05% to 10% by weight of the total composition of the diacyl peroxide described herein and from 0.01% to 10% by weight of a second peroxygen bleach. Furthermore, in another preferred embodiment of the present invention the composition also comprises a bleach activator. Such compositions deliver even more effective bleaching performance, especially at ambient temperature.

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The second peroxygen bleach to be used herein can be any peroxygen bleach known in the art, with the exception of the diacyl peroxide described herein. Such peroxygen bleaches include hydrogen peroxide, a water-soluble source thereof, or mixtures thereof. Hydrogen peroxide is most preferred for use in the compositions according to the present invention. Moreover, the presence of the second peroxygen bleach, preferably hydrogen peroxide, contributes to the excellent cleaning and bleaching benefits of the compositions. As used herein a hydrogen peroxide source refers to any compound which produces perhydroxyl ions when in contact with water.

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Suitable water-soluble sources of hydrogen peroxide for use herein include percarbonates, persilicate, persulphate such as monopersulfate, perborates, peroxyacids such as diperoxydodecandioic acid (DPDA), phthaloyl amino peroxycaproic acid (PAP), magnesium perphtalic acid, perlauric acid, perbenzoic

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and alkylperbenzoic acids, hydroperoxide like t-butyl hydroperoxide and mixtures thereof.

The compositions according to the present invention comprise from 0.01% to 10%, preferably from 0.5% to 8%, more preferably from 2% to 8%, and most preferably from 4% to 7% by weight of the composition of a second peroxygen bleach.

In a particularly preferred aspect of the present invention, the bleaching composition comprises a diacyl peroxide as described herein and a surfactant. The surfactant may be a surfactant system comprising more than one surfactant.

The compositions of the present invention are preferably aqueous liquid compositions. Said aqueous compositions are most preferably formulated to have pH from 2 to 5. The pH of the compositions of the present invention can be adjusted by using organic or inorganic acids known to those skilled in the art. Particularly suitable organic acids to be used herein are aryl and/or alkyl sulfonate, such as methane sulfonic acid or naphtalene disulfonic acid, citric acid, succinic acid, tartaric acid, sulphamic acid, glutaric acid, adipic acid and the like. Particularly suitable inorganic acids are sulfuric acid, phosphoric acid, nitric acid. The compositions used according to the process of the present invention are preferably aqueous compositions. The compositions used herein have a pH of from 0 to 12. Preferably the composition has pH of from 0 to 10, more preferably from 1 to 7, most preferably from 2 to 4.

25 By the term "improve colour safety" it is meant that the damage to dyes present on a fabric caused by the diacyl peroxide of the present invention is reduced when compared with damage cause by other bleaching agents, especially diaromatic peroxides, for example dibenzoyl peroxide i.e. improved fabric colour safety is equated to reduced fabric colour damage. The damage caused to the dyes is seen as a loss of colour intensity. Furthermore, this reduction in colour damage is seen even when the diacyl peroxide of the present invention is left in contact with the fabric, and thus the fabric dye, for prolonged periods at time before subsequent washing or rinsing of the fabric, e.g. 24 hours.

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It is speculated that colour safety is achieved due to the lower reactivity of the diacyl peroxide of the present invention versus other bleaching agents, especially diaromatic diacyl peroxide which are known to cause fabric colour damage.

The stain removal performance and fabric colour safety of the diacyl peroxide may be evaluated by the following test method. A diacyl peroxide according to the present invention, but preferably a composition comprising the diacyl peroxide, is first applied onto a fabric, preferably on the stained portion of said fabric, it is left to act thereon for 1 minute to 24 hours, preferably 5 to 10 minutes, after which the fabric is washed according to common washing conditions, at a temperature of from 30°C to 70°C for a period of time sufficient to bleach said fabric.

The stain removal performance may be evaluated by comparing side by side the soiled coloured fabric pre-treated with the diacyl peroxide composition or product, according to the present invention with those pre-treated with the reference containing it, e.g., the same compositions but without the diacyl peroxide of the present invention. For example, typical stains to be used in such a stain removal test method are commercially available from WFK (Krefeld, Germany) or from EMC (Empirical Manufacturing Company) Cincinnati, Ohio, USA, such as grass, coffee, tomato sauce, dirty motor oil, cosmetics, barbecue sauce, blood on different substrate/fabric, e.g., cotton (CW120) or polycotton (PCW28). A visual grading scale may be used to assign differences in panel score units (psu), in a range from 0 to 4 for the stain removal performance.

Colour safety may be evaluated by determination of the colour damage by side-by-side comparison of the soiled coloured fabric treated with the diacyl peroxide according to the present invention with those treated with the reference product, e.g., the same composition but without the diacyl peroxide of the present invention or a different bleaching agent, for example a diaromatic peroxide. Technical coloured swatches/fabrics suitable to be used in the colour damage test method herein, are commercially available from Tecnotessile (Prato, Italy) or EMC (Empirical Manufacturing Company) Cincinnati, Ohio, US. Typical colored fabrics/swatches used are for example the most sensitive to bleach like: C83 Reactive Blue®, C102 Reactive Blue®, C65 Reactive Violet®, C73 Direct Blue®, C105 Direct Brown®, C111 Direct Red®, C40 Sulphur Green®. A visual grading

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and/or instrumental methods with the "Hunterlab Tristimulus MINISCAN" may be used for the colour damage evaluation.

It is envisaged that the diacyl peroxide or a composition comprising it may be used as a pre-treatment, as an additive or a component of a detergent composition. Where the diacyl peroxide is used as a pre-treatment, it is preferred that the fabric to which the diacyl peroxide has been added is subsequently washed. By "washing" it is to be understood herein to simply rinse the fabrics with water, or the fabrics may be washed with a conventional detergent composition comprising at least one surface active agent, by means of a washing machine or simply by hand.

Where the diacyl peroxide is a component of a composition, the composition may be used in neat or dilute form. By "neat form" it is understood that the compositions is applied directly onto the fabric without undergoing any dilution.

Optionals

Where the present invention relates to the use of a composition comprising the diacyl peroxide, the composition may further comprise optional ingredients like bleach activators, surfactants, brighteners, chelating agents, radical scavengers, stabilisers, soil suspending polymers, soil release agents, dye transfer inhibiting agents, solvents, colourants, rheology modifiers, sud suppressors, catalysts, perfumes, or mixtures thereof.

As an optional but highly preferred ingredient, the compositions of the present invention comprise a bleach activator or mixtures thereof. By "bleach activator", it is meant herein a compound which reacts with hydrogen peroxide to form a peracid. The peracid thus formed constitutes the activated bleach. Particularly suitable bleach activators to be used herein are hydrophobic bleach activators, i.e., a bleach activator which is not substantially and stably miscible with water.

Suitable bleach activators to be used herein include those belonging to the class of esters, amides, imides, or anhydrides. Examples of suitable compounds of this type are disclosed in British Patent GB 1 586 769 and GB 2 143 231 and a method for their formation into a prilled form is described in European Published Patent Application EP-A-62 523. Suitable examples of such compounds to be

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used herein are tetracetyl ethylene diamine (TAED), sodium 3,5,5 trimethyl hexanoyloxybenzene sulphonate, diperoxy dodecanoic acid as described for instance in US 4 818 425 and nonylamide of peroxyadipic acid as described for instance in US 4 259 201 and alkyl-benzene sulphonates such as nnonanoyloxybenzenesulphonate (NOBS). Also suitable are N-acyl caprolactams selected from the group consisting of substituted or unsubstituted benzoyl caprolactam, octanovl caprolactam, nonanovi caprolactam, hexanoyl caprolactam, decanoyl caprolactam, undecenoyl caprolactam, formyl caprolactam, acetyl caprolactam, propanoyl caprolactam, butanoyl caprolactam pentanovl caprolactam or mixtures thereof. A particular family of bleach activators of interest was disclosed in EP 624 154, and particularly preferred in that family is acetyl triethyl citrate (ATC). Acetyl triethyl citrate has the advantage that it is environmental-friendly as it eventually degrades into citric acid and alcohol. Furthermore, acetyl triethyl citrate has a good hydrolytical stability in the product upon storage and it is an efficient bleach activator. Finally, it provides good building capacity to the composition.

The compositions according to the present invention may comprise from 0.01% to 30% by weight of the total composition of a bleach activator, or mixtures thereof, preferably from 0.5% to 10%, and more preferably from 3% to 7%.

The compositions according to the present invention may comprise a surfactant or mixtures thereof. Any surfactant known to those skilled in the art may be used herein including anionic surfactants, nonionic surfactants, zwitterionic surfactants, amphoteric surfactants and/or cationic surfactants up to a level of 50% by weight of the total composition.

The compositions according to the present invention may be formulated as solutions, emulsions, microemulsions, suspensions, pastes or powders.

For stability reasons, the compositions according to the present invention that may typically comprise a bleach activator, as described hereinbefore, are preferably formulated either as aqueous emulsions of said bleach activator in a matrix comprising water, the aliphatic diacyl peroxide, the second peroxygen bleach and an emulsifying surfactant system, or as microemulsions of said bleach activator in a matrix comprising water, the aliphatic diacyl peroxide, the second peroxygen bleach and a hydrophilic surfactant system.

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Preferred peroxygen bleach-containing compositions herein comprise an emulsifying surfactant system of at least two different surfactants, i.e., at least a hydrophobic surfactant having an HLB up to 9.5 or mixtures thereof, and at least a hydrophilic surfactant having an HLB above 10, or mixtures thereof, in order to emulsify the hydrophobic bleach activator where present. Preferred herein, said two different surfactants should have different HLB values (hydrophilic / lipophilic balance) in order to form stable compositions, and preferably the difference in value of the HLBs of said two surfactants is at least 1, preferably at least 2. Indeed, by appropriately combining at least two of said surfactants with different HLBs in water, emulsions will be formed which do not substantially separate into distinct layers, upon standing for at least two weeks at 40°C.

The preferred compositions according to the present invention comprise from 0.1 % to 50 %, more preferably from 1 % to 20 % and most preferably from 2 % to 10 %, by weight of surfactant. The surfactant may be hydrophilic or hydrophobic. The preferred compositions according to the present invention comprise at least from 0.01 %, preferably at least 2 % and more preferably at least 4 % of a hydrophobic surfactant and at least from 0.01 %, preferably at least 2%, and more preferably at least 4% of a hydrophilic surfactant.

The hydrophilic surfactant have an HLB above 10. Preferably hydrophilic nonionic surfactants having an HLB above 10 and more preferably above 10.5. Preferred hydrophobic surfactants are the hydrophobic nonionic surfactants. Said hydrophobic nonionic surfactants have an HLB of up to 9.5, preferably below 9.5, more preferably below 9. The hydrophobic nonionic surfactants to be used herein have excellent grease cutting properties, i.e., they have a solvent effect which contributes to hydrophobic soils removal.

30 Suitable nonionic surfactants for use herein include alkoxylated fatty alcohols preferably, fatty alcohol ethoxylates and/or propoxylates. Indeed, a great variety of such alkoxylated fatty alcohols are commercially available which have very different HLB values (hydrophilic / lipophilic balance). The HLB values of such alkoxylated nonionic surfactants depend essentially on the chain length of the fatty alcohol, the nature of the alkoxylation and the degree of alkoxylation. Hydrophilic nonionic surfactants tend to have a high degree of alkoxylation and a

short chain fatty alcohol, while hydrophobic surfactants tend to have a low degree of alkoxylation and a long chain fatty alcohol. Surfactant catalogs are available which list a number of surfactants including nonionics, together with their respective HLB values.

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Suitable chemical processes for preparing the nonionic surfactants for use herein include condensation of corresponding alcohols with alkylene oxide, in the desired proportions. Such processes are well-known to the man skilled in the art and have been extensively described in the art. As an alternative, a great variety of alkoxylated alcohols suitable for use herein is commercially available from various suppliers.

Preferred hydrophobic nonionic surfactants to be used in the present invention

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are surfactants having an HLB up to 9 and being according to the formula RO- $(C_2H_4O)_n(C_3H_6O)_mH$, wherein R is a C_6 to C_{22} alkyl chain or a C_6 to C_{28} alkyl benzene chain, and wherein n+m is from 0.5 to 5 and n is from 0 to 5 and m is from 0 to 5 and preferably n+m is from 0.5 to 4.5 and, n and m are from 0 to 4.5. The preferred R chains for use herein are the C_8 to C_{22} alkyl chains. Accordingly, suitable hydrophobic nonionic surfactants for use herein are Dobanol \overline{R} 91-2.5 (HLB= 8.1; R is a mixture of C₉ and C₁₁ alkyl chains, n is 2.5 and m is 0), or Lutensol R TO3 (HLB=8; R is a mixture of C_{13} and C_{15} alkyl chains, n is 3 and m is 0), or Tergitol $^{\rm R}$ 25L3 (HLB= 7.7; R is in the range of $^{\rm C}$ 12 to C₁₅ alkyl chain length, n is 3 and m is 0), or Dobanol R 23-3 (HLB=8.1; R is a mixture of C₁₂ and C₁₃ alkyl chains, n is 3 and m is 0), or Dobanol R 23-2 (HLB= 6.2; R is a mixture of C₁₂ and C₁₃ alkyl chains, n is 2 and m is 0), or mixtures thereof. Preferred herein are Dobanol R 23-3, or Dobanol R 23-2, These Dobanol R surfactants are Lutensol R TO3, or mixtures thereof. These Lutensol R surfactants are commercially available from SHELL. commercially available from BASF and these Tergitol R surfactants are commercially available from UNION CARBIDE. Other suitable hydrophobic nonionic surfactants to be used herein are non alkoxylated surfactants. An example is Dobanol R 23 (HLB<3).

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Preferred hydrophilic nonionic surfactants to be used herein are surfactants having an HLB above 10 and being according to the formula RO- $(C_2H_4O)_n(C_3H_6O)_mH$, wherein R is a C_6 to C_{22} alkyl chain or a C_6 to C_{28} alkyl benzene chain, and

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wherein n+m is from 5 to 11 and n is from 0 to 11 and m is from 0 to 11, preferably n+m is from 6 to 10 and, n and m are from 0 to 10. Throughout this description n and m refer to the average degree of the ethoxylation/propoxylation. preferred R chains for use herein are the C₈ to C₂₂ alkyl chains. Accordingly, suitable hydrophilic nonionic surfactants for use herein are Dobanol R 23-6.5 (HLB=11.9 ; R is a mixture of C_{12} and C_{13} alkyl chains, n is 6.5 and m is 0), or Dobanol R 25-7 (HLB=12 ; R is a mixture of C_{12} to C_{15} alkyl chains, n is 7 and m is 0), or Dobanol R 45-7 (HLB=11.6 ; R is a mixture of C_{14} and C_{15} alkyl chains, n is 7 and m is 0), or Dobanol R 91-5 (HLB=11.6 ; R is a mixture of C9 to C_{11} alkyl chains, n is 5 and m is 0), or Dobanol R 91-6 (HLB=12.5; R is a mixture of C_9 to C₁₁ alkyl chains, n is 6 and m is 0), or Dobanol R 91-8 (HLB=13.7; R is a mixture of C₉ to C₁₁ alkyl chains, n is 8 and m is 0), or Dobanol R 91-10 (HLB= 14.2; R is a mixture of C9 to C11 alkyl chains, n is 10 and m is 0), or mixtures thereof. Preferred herein are Dobanol R 91-10, or Dobanol R 45-7, Dobanol R 23-6.5, or mixtures thereof. These Dobanol R surfactants are commercially available from SHELL.

Apart from the hydrophilic nonionic surfactants, other hydrophilic surfactants may also be used in the compositions of the present invention such as anionic surfactants described hereinafter and/or polyhydroxy fatty acid amide surfactant, or mixtures thereof, according to the formula

$$R^2 - C(O) - N(R^1) - Z$$

wherein R¹ is H, or C₁-C₄ alkyl, C₁-C₄ hydrocarbyl, 2-hydroxy ethyl, 2-hydroxy propyl or a mixture thereof, R² is C₅-C₃₁ hydrocarbyl, and Z is a polyhydroxyhydrocarbyl having a linear hydrocarbyl chain with at least 3 hydroxyls directly connected to the chain, or an alkoxylated derivative thereof.

Preferably, R¹ is C₁-C₄ alkyl, more preferably C₁ or C₂ alkyl and most preferably methyl, R² is a straight chain C₇-C₁₉ alkyl or alkenyl, preferably a straight chain C₉-C₁₈ alkyl or alkenyl, more preferably a straight chain C₁₁-C₁₈ alkyl or alkenyl, and most preferably a straight chain C₁₁-C₁₄ alkyl or alkenyl, or mixtures thereof. Z preferably will be derived from a reducing sugar in a reductive amination reaction; more preferably Z is a glycityl. Suitable reducing sugars

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include glucose, fructose, maltose, lactose, galactose, mannose and xylose. As raw materials, high dextrose corn syrup, high fructose corn syrup, and high maltose corn syrup can be utilised as well as the individual sugars listed above. These corn syrups may yield a mix of sugar components for Z. It should be understood that it is by no means intended to exclude other suitable raw materials. Z preferably will be selected from the group consisting of -CH₂-(CHOH)_n-CH₂OH, -CH(CH₂OH)-(CHOH)_{n-1}-CH₂OH, -CH₂-(CHOH)₂-(CHOH)-CH₂OH, where n is an integer from 3 to 5, inclusive, and R' is H or a cyclic or aliphatic monosaccharide, and alkoxylated derivatives thereof. Most preferred are glycityls wherein n is 4, particularly CH₂-(CHOH)₄-CH₂OH.

In the formula R^2 - C(O) - $N(R^1)$ - Z, R^1 can be, for example, N-methyl, N-ethyl, N-propyl, N-isopropyl, N-butyl, N-2-hydroxy ethyl, or N-2-hydroxy propyl. R^2 - C(O) - N< can be, for example, cocamide, stearamide, oleamide, lauramide, myristamide, capricamide, palmitamide, tallowamide and the like. Z can be 1-deoxyglucityl, 2-deoxyfructityl, 1-deoxymaltityl, 1-deoxymaltotriotityl and the like.

Suitable polyhydroxy fatty acid amide surfactants to be used herein may be commercially available under the trade name HOE® from Hoechst.

Methods for making polyhydroxy fatty acid amide surfactants are known in the art. In general, they can be made by reacting an alkyl amine with a reducing sugar in a reductive amination reaction to form a corresponding N-alkyl polyhydroxyamine, and then reacting the N-alkyl polyhydroxyamine with a fatty aliphatic ester or triglyceride in a condensation/amidation step to form the N-alkyl, N-polyhydroxy fatty acid amide product. Processes for making compositions containing polyhydroxy fatty acid amides are disclosed for example in GB patent specification 809,060, published February 18, 1959, by Thomas Hedley & Co., Ltd., US patent 2,965,576, issued December 20, 1960 to E.R. Wilson, US patent 2,703,798, Anthony M. Schwartz, issued March 8, 1955, US patent 1,985,424, issued December 25, 1934 to Piggott and WO92/06070, each of which is incorporated herein by reference.

In a particularly preferred embodiment of the present invention, wherein the compositions comprise acetyl triethyl citrate as the bleach activator, an adequate

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surfactant system, would comprise a hydrophobic nonionic surfactant with for instance an HLB of 6, such as a Dobanol $^{\rm R}$ 23-2 and a hydrophilic nonionic surfactant with for instance an HLB of 15, such as a Dobanol $^{\rm R}$ 91-10. Other suitable nonionic surfactant systems comprise for example a Dobanol $^{\rm R}$ 23-6.5 (HLB about 12) and a Dobanol $^{\rm R}$ 23 (HLB below 6) or a Dobanol $^{\rm R}$ 45-7 (HLB=11.6) and a Dobanol 23-3 (HLB=8.1).

In the embodiment of the present invention where the compositions are formulated as emulsions said compositions are opaque. In centrifugation examination, it was observed that said emulsions herein showed no phase separation after 15 minutes at 6000 rpm. Under microscopic examination, said emulsions appeared as a dispersion of droplets in a matrix.

In the embodiment of the present invention where the compositions of the present invention are formulated as microemulsions, said bleaching microemulsions according to the present invention comprise a hydrophilic surfactant system comprising at least two different surfactants like a nonionic surfactant and an anionic surfactant.

Suitable hydrophilic surfactants to be used herein are those hydrophilic surfactants mentioned herein. A key factor in order to stably incorporate for example the bleach activator in said microemulsions is that at least one of said surfactants of the hydrophilic surfactant system must have a different HLB value to that of the bleach activator. Indeed, if all said surfactants had the same HLB value as that of the activator, a continuous single phase might be formed, thus lowering the chemical stability of the bleach/bleach activator system. Preferably, at least one of said surfactants has an HLB value which differs by at least 1.0 HLB unit, preferably 2.0 to that of said bleach activator.

Suitable anionic surfactants to be used herein include water-soluble salts or acids of the formula ROSO₃M or RSO₃M wherein R preferably is a C₁₀-C₂₄ hydrocarbyl, preferably an alkyl or hydroxyalkyl having a C₁₀-C₂₀ alkyl component, more preferably a C₁₂-C₁₈ alkyl or hydroxyalkyl, and M is H or a cation, e.g., an alkali metal cation (e.g., sodium, potassium, lithium), or ammonium or substituted ammonium (e.g., methyl-, dimethyl-, and trimethyl ammonium cations and quaternary ammonium cations, such as tetramethyl-

ammonium and dimethyl piperdinium cations and quaternary ammonium cations derived from alkylamines such as ethylamine, diethylamine, triethylamine, and mixtures thereof, and the like). Typically, alkyl chains of C_{12} - $_{16}$ are preferred for lower wash temperatures (e.g., below about 50°C) and C_{16} - $_{18}$ alkyl chains are preferred for higher wash temperatures (e.g., above about 50°C).

Other suitable anionic surfactants for use herein are water-soluble salts or acids of the formula RO(A)_mSO₃M wherein R is an unsubstituted C₁₀-C₂₄ alkyl or hydroxyalkyl group having a C₁₀-C₂₄ alkyl component, preferably a C₁₂-C₂₀ alkyl or hydroxyalkyl, more preferably C12-C18 alkyl or hydroxyalkyl, A is an ethoxy or propoxy unit, m is greater than zero, typically between about 0.5 and about 6, more preferably between about 0.5 and about 3, and M is H or a cation which can be, for example, a metal cation (e.g., sodium, potassium, lithium, calcium, magnesium, etc.), ammonium or substituted-ammonium cation. Alkyl ethoxylated sulfates as well as alkyl propoxylated sulfates are contemplated herein. Specific examples of substituted ammonium cations include methyl-, dimethyl-, trimethyl-ammonium and quaternary ammonium cations, such as tetramethyl-ammonium, dimethyl piperdinium and cations derived from alkanolamines such as ethylamine, diethylamine, triethylamine, mixtures thereof, and the like. Exemplary surfactants are C₁₂-C₁₈ alkyl polyethoxylate (1.0) sulfate, C_{12} - $C_{18}E(1.0)M$), C_{12} - C_{18} alkyl polyethoxylate (2.25) sulfate, C_{12} - $C_{18}E(2.25)M$), $C_{12}-C_{18}$ alkyl polyethoxylate (3.0) sulfate $C_{12}-C_{18}E(3.0)$, and C₁₂-C₁₈ alkyl polyethoxylate (4.0) sulfate C₁₂-C₁₈E(4.0)M), wherein M is conveniently selected from sodium and potassium.

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Other anionic surfactants useful for detersive purposes can also be used herein. These can include salts (including, for example, sodium, potassium, ammonium, and substituted ammonium salts such as mono-, di- and triethanolamine salts) of soap, C_9 - C_{20} linear alkylbenzenesulfonates, C_8 - C_{22} primary or secondary alkanesulfonates, C_8 - C_{24} olefinsulfonates, sulfonated polycarboxylic acids prepared by sulfonation of the pyrolyzed product of alkaline earth metal citrates, e.g., as described in British patent specification No. 1,082,179, C_8 - C_{24} alkylpolyglycolethersulfates (containing up to 10 moles of ethylene oxide); alkyl ester sulfonates such as C_{14-16} methyl ester sulfonates; acyl glycerol sulfonates, fatty oleyl glycerol sulfates, alkyl phenol ethylene oxide ether sulfates, paraffin sulfonates, alkyl phosphates, isethionates such as the acyl isethionates, N-acyl

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taurates, alkyl succinamates and sulfosuccinates, monoesters of sulfosuccinate (especially saturated and unsaturated C12-C18 monoesters) diesters of sulfosuccinate (especially saturated and unsaturated C6-C14 diesters), sulfates of alkylpolysaccharides such as the sulfates of alkylpolyglucoside (the nonionic nonsulfated compounds being described below), branched primary alkyl sulfates, alkyl polyethoxy carboxylates such those of the formula ${\rm RO(CH_2CH_2O)_kCH_2COO-M}^{+}$ wherein R is a ${\rm C_8^-C_{22}}$ alkyl, k is an integer from 0 to 10, and M is a soluble salt-forming cation. Resin acids and hydrogenated resin acids are also suitable, such as rosin, hydrogenated rosin, and resin acids and hydrogenated resin acids present in or derived from tall oil. examples are given in "Surface Active Agents and Detergents" (Vol. I and II by Schwartz, Perry and Berch). A variety of such surfactants are also generally disclosed in U.S. Patent 3,929,678, issued December 30, 1975 to Laughlin, et al. at Column 23, line 58 through Column 29, line 23 (herein incorporated by reference).

Particularly preferred anionic surfactants for use in the compositions described herein are alkali or alkaline earth metal, preferably sodium, paraffin sulphonates (e.g. NaPS available from for example Hoescht or Huls).

Other suitable anionic surfactants to be used herein also include acyl sarcosinate or mixtures thereof, in its acid and/or salt form, preferably long chain acyl sarcosinates having the following formula:

wherein M is hydrogen or a cationic moiety and wherein R is an alkyl group of from 11 to 15 carbon atoms, preferably of from 11 to 13 carbon atoms. Preferred M are hydrogen and alkali metal salts, especially sodium and potassium. Said acyl sarcosinate surfactants are derived from natural fatty acids and the amino-acid sarcosine (N-methyl glycine). They are suitable to be used as aqueous solution of

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their salt or in their acidic form as powder. Being derivatives of natural fatty acids, said acyl sarcosinates are rapidly and completely biodegradable and have good skin compatibility.

Accordingly, particularly preferred long chain acyl sarcosinates to be used herein include C₁₂ acyl sarcosinate (i.e. an acyl sarcosinate according to the above formula wherein M is hydrogen and R is an alkyl group of 11 carbon atoms) and C₁₄ acyl sarcosinate (i.e. an acyl sarcosinate according to the above formula wherein M is hydrogen and R is an alkyl group of 13 carbon atoms). C₁₂ acyl sarcosinate is commercially available, for example, as Hamposyl L-30[®] supplied by Hampshire. C₁₄ acyl sarcosinate is commercially available, for example, as Hamposyl M-30[®] supplied by Hampshire.

Suitable other hydrophilic nonionic surfactants for use in the microemulsions herein include the hydrophilic nonionic surfactants as defined hereinbefore for the emulsions.

The preferred making of the microemulsions of the present invention includes premixing the surfactants with water and subsequently adding the other ingredients including the aliphatic diacyl peroxide, the second peroxygen bleach, e.g., hydrogen peroxide, and other ingredients like a bleach activator if present. Irrespective of this preferred order of addition, it is important that during the mixing of the ingredients, the microemulsions be constantly kept under stirring under relatively high stirring energies, preferably 30 minutes at 750 rpm, most preferably 30 minutes at 1000 rpm.

In the embodiment of the present invention where the compositions are formulated as microemulsions said compositions are macroscopically transparent in the absence of opacifiers and colourants. In centrifugation examination, it was observed that said microemulsions herein showed no phase separation after 15 minutes at 6000 rpm. Under microscopic examination, said microemulsions appeared as a dispersion of droplets in a matrix. We have observed that the particles had a size which is typically around or below 3 micron diameter.

Accordingly, said bleaching compositions of the present invention may be packaged in a given deformable container/bottle without compromising the stability of said container/bottle comprising it upon standing, for long periods of time.

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Suitable chelating agents to be used herein include chelating agents selected from the group of phosphonate chelating agents, amino carboxylate chelating agents, polyfunctionally-substituted aromatic chelating agents, and further chelating agents like glycine, salicylic acid, aspartic acid, glutamic acid, malonic acid, or mixtures thereof. Chelating agents when used, are typically present herein in amounts ranging from 0.001% to 5% by weight of the total composition and preferably from 0.05% to 2% by weight.

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Suitable phosphonate chelating agents to be used herein may include ethydronic acid as well as amino phosphonate compounds, including amino alkylene poly (alkylene phosphonate), alkali metal ethane 1-hydroxy diphosphonates, nitrilo trimethylene phosphonates, ethylene diamine tetra methylene phosphonates, and diethylene triamine penta methylene phosphonates. In a preferred embodiment, the phosphonate chelant is alkali metal ethane 1-hydroxy diphosphonates (HEDP). The phosphonate compounds may be present either in their acid form or as salts of different cations on some or all of their acid functionalities. Preferred phosphonate chelating agents to be used herein are diethylene triamine penta methylene phosphonates. Such phosphonate chelating agents are commercially available from Monsanto under the trade name DEQUEST[®].

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The most preferred phosphonate chelating agent to be used herein is aminotri(methylene phosphonic acid), herein referred to as ATMP. Indeed, it has been found that the addition of ATMP, i.e. the compound of formula:

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in a liquid composition of the present invention considerably reduces the damage otherwise associated with the pretreatment of fabrics with peroxygen bleach-containing compositions, especially those fabrics which contain metal ions, such as copper, iron, chromium, and manganese.

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Polyfunctionally-substituted aromatic chelating agents may also be useful in the compositions herein. See U.S. patent 3,812,044, issued May 21, 1974, to Connor et al. Preferred compounds of this type in acid form are dihydroxydisulfobenzenes such as 1,2-dihydroxy -3,5-disulfobenzene.

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A preferred biodegradable chelating agent for use herein is ethylene diamine N,N'-disuccinic acid, or alkali metal, or alkaline earth, ammonium or substitutes ammonium salts thereof or mixtures thereof. Ethylenediamine N,N'- disuccinic acids, especially the (S,S) isomer have been extensively described in US patent 4, 704, 233, November 3, 1987, to Hartman and Perkins. Ethylenediamine N,N'-disuccinic acids is, for instance, commercially available under the tradename ssEDDS® from Palmer Research Laboratories.

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Suitable amino carboxylates to be used herein include ethylene diamine tetra acetates, diethylene triamine pentaacetates, diethylene triamine pentaacetate (DTPA),N- hydroxyethylethylenediamine triacetates, nitrilotri-acetates, ethylenediamine tetrapropionates, triethylenetetraaminehexa-acetates, ethanoldiglycines, propylene diamine tetracetic acid (PDTA) and methyl glycine di-acetic acid (MGDA), both in their acid form, or in their alkali metal, ammonium, and substituted ammonium salt forms. Particularly suitable amino carboxylates to be used herein are diethylene triamine penta acetic acid, propylene diamine tetracetic acid (PDTA) which is, for instance, commercially available from BASF under the trade name Trilon FS® and methyl glycine di-acetic acid (MGDA).

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Another preferred chelating agent for use herein is of the formula:

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 $R_1R_2R_3R_4$ OH COOH R_5 R_6 $R_1R_2R_3R_4$ $R_1R_2R_3R_4$

wherein R_1 , R_2 , R_3 , and R_4 are independently selected from the group consisting of -H, alkyl, alkoxy, aryl, aryloxy, -Cl, -Br, -NO₂, -C(O)R', and -SO₂R"; wherein R' is selected from the group consisting of -H, -OH, alkyl, alkoxy, aryl, and aryloxy; R" is selected from the group consisting of alkyl, alkoxy, aryl, and aryloxy; and R_5 , R_6 , R_7 , and R_8 are independently selected from the group consisting of -H and alkyl.

Particularly preferred chelating agents to be used herein are ATMP, diethylene triamine methylene phosphonate, ethylene N,N'-disuccinic acid, diethylene triamine pantaacetate, glycine, salicylic acid, aspartic acid, glutamic acid, malonic acid or mixtures thereof and highly preferred is ATMP.

Suitable radical scavengers for use herein include the well-known substituted mono and dihydroxy benzenes and their analogs, alkyl and aryl carboxylates and mixtures thereof. Preferred such radical scavengers for use herein include di-tert-butyl hydroxy toluene (BHT), hydroquinone, di-tert-butyl hydroquinone, mono-tert-butyl hydroquinone, tert-butyl-hydroxy anysole, benzoic acid, toluic acid, catechol, t-butyl catechol, benzylamine, 1,1,3-tris(2-methyl-4-hydroxy-5-t-butylphenyl) butane, n-propyl-gallate or mixtures thereof and highly preferred is di-tert-butyl hydroxy toluene. Radical scavengers when used, are typically present herein in amounts ranging from 0.001% to 2% by weight of the total composition and preferably from 0.001% to 0.5% by weight.

The presence of chelating agents, especially ATMP, and/or radical scavengers allows to contribute to the safety profile of the compositions of the present invention suitable for pretreating a soiled colored fabric upon prolonged contact times before washing said fabric.

Other stabilizers like inorganic stabilizers may be used herein. Examples of inorganic stabilizers include sodium stannate and various alkali metal

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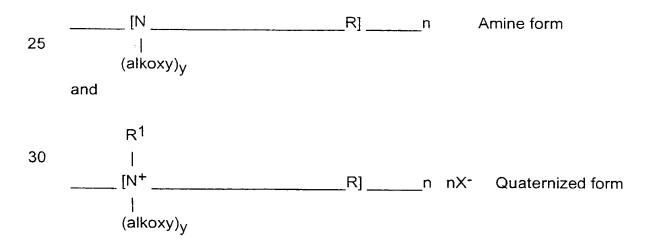
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phosphates such as the well-known sodium tripolyphosphates, sodium pyrophosphate and sodium orthophosphate.

The compositions according to the present invention may further comprise a foam suppressor such as 2-alkyl alkanol, or mixtures thereof, as an optional ingredient. Particularly suitable to be used in the present invention are the 2-alkyl alkanols having an alkyl chain comprising from 6 to 16 carbon atoms, preferably from 8 to 12 and a terminal hydroxy group, said alkyl chain being substituted in the α position by an alkyl chain comprising from 1 to 10 carbon atoms, preferably from 2 to 8 and more preferably 3 to 6. Such suitable compounds are commercially available, for instance, in the Isofol® series such as Isofol® 12 (2-butyl octanol) or Isofol® 16 (2-hexyl decanol). Typically, the compositions of the present invention comprise up to 2 % by weight of the total composition of a 2-alkyl alkanol, or mixtures thereof, preferably from 0.05 % to 1.5 % and more preferably from 0.1 % to 0.8 %.

The compositions according to the present invention may further comprise a soil suspending polymer or mixtures thereof, as optional ingredient. Any soil suspending polymer known to those skilled in the art may also be used herein. Particularly suitable are polyamine polymers such as polyalkoxylated polyamines. Such materials can conveniently be represented as molecules of the empirical structures with repeating units:



wherein R is a hydrocarbyl group, usually of 2-6 carbon atoms; R¹ may be a C₁-C₂₀ hydrocarbon; the alkoxy groups are ethoxy, propoxy, and the like, and y is 2-

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30, most preferably from 10-20; n is an integer of at least 2, preferably from 2-20, most preferably 3-5; and X^- is an anion such as halide or methylsulfate, resulting from the quaternization reaction.

The most highly preferred polyamines for use herein are the so-called ethoxylated polyethylene amines, i.e., the polymerized reaction product of ethylene oxide with ethyleneimine, having the general formula:

when y = 2-30. Particularly preferred for use herein is an ethoxylated polyethylene amine, in particular ethoxylated tetraethylenepentamine, and quaternized ethoxylated hexamethylene diamine.

It has surprisingly been found that said soil suspending polyamine polymers contribute to the benefits of the present invention, i.e., that when added on top of said aliphatic diacyl peroxide, they further improve the stain removal performance of a composition comprising them, especially under laundry pretreatment conditions, as described herein. Indeed, they allow to improve the stain removal performance on a variety of stains including greasy stains, enzymatic stains, clay/mud-stains as well as on bleachable stains.

Typically, the compositions comprise up to 10% by weight of the total composition of such a soil suspending polyamine polymer or mixtures thereof, preferably from 0.1% to 5% and more preferably from 0.3% to 2%.

The compositions herein may also comprise other polymeric soil release agents known to those skilled in the art. Such polymeric soil release agents are characterised by having both hydrophilic segments, to hydrophilize the surface of hydrophobic fibres, such as polyester and nylon, and hydrophobic segments, to deposit upon hydrophobic fibres and remain adhered thereto through completion of washing and rinsing cycles and, thus, serve as an anchor for the hydrophilic

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segments. This can enable stains occurring subsequent to treatment with the soil release agent to be more easily cleaned in later washing procedures.

The polymeric soil release agents useful herein especially include those soil release agents having: (a) one or more nonionic hydrophile components consisting essentially of (i) polyoxyethylene segments with a degree of polymerization of at least 2, or (ii) oxypropylene or polyoxypropylene segments with a degree of polymerization of from 2 to 10, wherein said hydrophile segment does not encompass any oxypropylene unit unless it is bonded to adjacent moieties at each end by ether linkages, or (iii) a mixture of oxyalkylene units comprising oxyethylene and from 1 to about 30 oxypropylene units wherein said mixture contains a sufficient amount of oxyethylene units such that the hydrophile component has hydrophilicity great enough to increase the hydrophilicity of conventional polyester synthetic fiber surfaces upon deposit of the soil release agent on such surface, said hydrophile segments preferably comprising at least about 25% oxyethylene units and more preferably, especially for such components having about 20 to 30 oxypropylene units, at least about 50% oxyethylene units; or (b) one or more hydrophobe components comprising (i) C3 oxyalkylene terephthalate segments, wherein, if said hydrophobe components oxyethylene terephthalate, the ratio of terephthalate:C3 oxyalkylene terephthalate units is about 2:1 or lower, (ii) C4-C6 alkylene or oxy C₄-C₆ alkylene segments, or mixtures therein, (iii) poly (vinyl ester) segments, preferably polyvinyl acetate), having a degree of polymerization of at least 2, or (iv) C₁-C₄ alkyl ether or C₄ hydroxyalkyl ether substituents, or mixtures therein, wherein said substituents are present in the form of C₁-C₄ alkyl ether or C₄ hydroxyalkyl ether cellulose derivatives, or mixtures therein, and such cellulose derivatives are amphiphilic, whereby they have a sufficient level of C₁-C₄ alkyl ether and/or C₄ hydroxyalkyl ether units to deposit upon conventional polyester synthetic fiber surfaces and retain a sufficient level of hydroxyls, once adhered to such conventional synthetic fiber surface, to increase fiber surface hydrophilicity, or a combination of (a) and (b).

Typically, the polyoxyethylene segments of (a)(i) will have a degree of polymerization of from about 1 to about 200, although higher levels can be used, preferably from 3 to about 150, more preferably from 6 to about 100. Suitable oxy C₄-C₆ alkylene hydrophobe segments include, but are not limited to, end-

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caps of polymeric soil release agents such as $MO_3S(CH_2)_nOCH_2CH_2O_7$, where M is sodium and n is an integer from 4-6, as disclosed in U.S. Patent 4,721,580, issued January 26, 1988 to Gosselink.

Polymeric soil release agents useful in the present invention also include cellulosic derivatives such as hydroxyether cellulosic polymers, co-polymeric blocks of ethylene terephthalate or propylene terephthalate with polyethylene oxide or polypropylene oxide terephthalate, and the like. Such agents are commercially available and include hydroxyethers of cellulose such as METHOCEL (Dow). Cellulosic soil release agents for use herein also include those selected from the group consisting of C₁-C₄ alkyl and C₄ hydroxyalkyl cellulose; see U.S. Patent 4,000,093, issued December 28, 1976 to Nicol, et al.

Soil release agents characterised by poly(vinyl ester) hydrophobe segments include graft co-polymers of poly(vinyl ester), e.g., C_1 - C_6 vinyl esters, preferably poly(vinyl acetate) grafted onto polyalkylene oxide backbones, such as polyethylene oxide backbones. See European Patent Application 0 219 048, published April 22, 1987 by Kud, et al. Commercially available soil release agents of this kind include the SOKALAN type of material, e.g., SOKALAN HP-22, available from BASF (West Germany).

One type of preferred soil release agent is a co-polymer having random blocks of ethylene terephthalate and polyethylene oxide (PEO) terephthalate. The molecular weight of this polymeric soil release agent is in the range of from about 25,000 to about 55,000. See U.S. Patent 3,959,230 to Hays, issued May 25, 1976 and U.S. Patent 3,893,929 to Basadur issued July 8, 1975.

Another preferred polymeric soil release agent is a polyester with repeat units of ethylene terephthalate units which contains 10-15% by weight of ethylene terephthalate units together with 90-80% by weight of polyoxyethylene terephthalate units, derived from a polyoxyethylene glycol of average molecular weight 300-5,000. Examples of this polymer include the commercially available material ZELCON 5126 (from Dupont) and MILEASE T (from ICI). See also U.S. Patent 4,702,857, issued October 27, 1987 to Gosselink.

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Another preferred polymeric soil release agent is a sulfonated product of a substantially linear ester oligomer comprised of an oligomeric ester backbone of terephthaloyl and oxyalkyleneoxy repeat units and terminal moieties covalently attached to the backbone. These soil release agents are fully described in U.S. Patent 4,968,451, issued November 6, 1990 to J.J. Scheibel and E.P. Gosselink. Other suitable polymeric soil release agents include the terephthalate polyesters of U.S. Patent 4,711,730, issued December 8, 1987 to Gosselink et al, the anionic end-capped oligomeric esters of U.S. Patent 4,721,580, issued January 26, 1988 to Gosselink, and the block polyester oligomeric compounds of U.S. Patent 4,702,857, issued October 27, 1987 to Gosselink.

Preferred polymeric soil release agents also include the soil release agents of U.S. Patent 4,877,896, issued October 31, 1989 to Maldonado et al, which discloses anionic, especially sulfoaroyl, end-capped terephthalate esters.

Still another preferred soil release agent is an oligomer with repeat units of terephthaloyl units, sulfoisoterephthaloyl units, oxyethyleneoxy and oxy-1,2-propylene units. The repeat units form the backbone of the oligomer and are preferably terminated with modified isethionate end-caps. A particularly preferred soil release agent of this type comprises about one sulfoisophthaloyl unit, 5 terephthaloyl units, oxyethyleneoxy and oxy-1,2-propyleneoxy units in a ratio of from about 1.7 to about 1.8, and two end-cap units of sodium 2-(2-hydroxyethoxy)-ethanesulfonate. Said soil release agent also comprises from about 0.5% to about 20%, by weight of the oligomer, of a crystalline-reducing stabilizer, preferably selected from the group consisting of xylene sulfonate, cumene sulfonate, toluene sulfonate, and mixtures thereof. See U.S. Pat. No. 5,415,807, issued May 16, 1995, to Gosselink et al.

If utilised, soil release agents will generally comprise from about 0.01% to about 10.0%, by weight, of the detergent compositions herein, typically from about 0.1% to about 5%, preferably from about 0.2% to about 3.0%.

The compositions of the present invention may also include one or more materials effective for inhibiting the transfer of dyes from one dyed surface to another during the cleaning process. Generally, such dye transfer inhibiting agents include polyvinyl pyrrolidone polymers, polyamine N-oxide polymers, co-

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polymers of N-vinylpyrrolidone and N-vinylimidazole, manganese phthalocyanine, peroxidases, and mixtures thereof. If used, these agents typically comprise from about 0.01% to about 10% by weight of the composition, preferably from about 0.01% to about 5%, and more preferably from about 0.05% to about 2%.

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More specifically, the polyamine N-oxide polymers preferred for use herein contain units having the following structural formula: R-A_X-P; wherein P is a polymerizable unit to which an N-O group can be attached or the N-O group can form part of the polymerizable unit or the N-O group can be attached to both units; A is one of the following structures: -NC(O)-, -C(O)O-, -S-, -O-, -N=; x is 0 or 1; and R is aliphatic, ethoxylated aliphatics, aromatics, heterocyclic or alicyclic groups or any combination thereof to which the nitrogen of the N-O group can be attached or the N-O group is part of these groups. Preferred polyamine N-oxides are those wherein R is a heterocyclic group such as pyridine, pyrrole, imidazole, pyrrolidine, piperidine and derivatives thereof.

The N-O group can be represented by the following general structures:

$$(R_1)_X - N - (R_2)_y;$$
 $= N - (R_1)_X$ $(R_3)_Z$

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wherein R_1 , R_2 , R_3 are aliphatic, aromatic, heterocyclic or alicyclic groups or combinations thereof; x, y and z are 0 or 1; and the nitrogen of the N-O group can be attached or form part of any of the aforementioned groups. The amine oxide unit of the polyamine N-oxides has a pKa <10, preferably pKa <7, more preferred pKa <6.

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Any polymer backbone can be used as long as the amine oxide polymer formed is water-soluble and has dye transfer inhibiting properties. Examples of suitable polymeric backbones are polyvinyls, polyalkylenes, polyesters, polyethers, polyamide, polyimides, polyacrylates and mixtures thereof. These polymers include random or block co-polymers where one monomer type is an amine Noxide and the other monomer type is an Noxide. The amine Noxide polymers typically have a ratio of amine to the amine Noxide of 10:1 to 1:1,000,000.

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However, the number of amine oxide groups present in the polyamine oxide polymer can be varied by appropriate co-polymerization or by an appropriate degree of N-oxidation. The polyamine oxides can be obtained in almost any degree of polymerization. Typically, the average molecular weight is within the range of 500 to 1,000,000; more preferred 1,000 to 500,000; most preferred 5,000 to 100,000. This preferred class of materials can be referred to as "PVNO". The most preferred polyamine N-oxide useful in the detergent compositions herein is poly(4-vinylpyridine-N-oxide) which as an average molecular weight of about 50,000 and an amine to amine N-oxide ratio of about 1:4.

Co-polymers of N-vinylpyrrolidone and N-vinylimidazole polymers (referred to as a class as "PVPVI") are also preferred for use herein. Preferably the PVPVI has an average molecular weight range from 5,000 to 1,000,000, more preferably from 5,000 to 200,000, and most preferably from 10,000 to 20,000. (The average molecular weight range is determined by light scattering as described in Barth, et al., Chemical Analysis, Vol 113. "Modern Methods of Polymer Characterization", the disclosures of which are incorporated herein by reference.) The PVPVI copolymers typically have a molar ratio of N-vinylimidazole to N-vinylpyrrolidone from 1:1 to 0.2:1, more preferably from 0.8:1 to 0.3:1, most preferably from 0.6:1 to 0.4:1. These co-polymers can be either linear or branched.

The present invention compositions may also employ a polyvinylpyrrolidone ("PVP") having an average molecular weight of from about 5,000 to about 400,000, preferably from about 5,000 to about 200,000, and more preferably from about 5,000 to about 50,000. PVP's are known to persons skilled in the detergent field; see, for example, EP-A-262,897 and EP-A-256,696, incorporated herein by reference. Compositions containing PVP can also contain polyethylene glycol ("PEG") having an average molecular weight from about 500 to about 100,000, preferably from about 1,000 to about 10,000. Preferably, the ratio of PEG to PVP on a ppm basis delivered in wash solutions is from about 2:1 to about 50:1, and more preferably from about 3:1 to about 10:1.

If high sudsing is desired, suds boosters such as C_{10} - C_{16} alkanolamides can be incorporated into the compositions, typically at 1%-10% levels. The C_{10} - C_{14} monoethanol and diethanol amides illustrate a typical class of such suds

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boosters. Use of such suds boosters with high sudsing adjunct surfactants such as the amine oxides, betaines and sultaines noted above is also advantageous. If desired, soluble magnesium salts such as MgCl₂, MgSO₄, and the like, can be added at levels of, for example, 0.1%-2%, to provide additional suds and to enhance grease removal performance.

Any optical brighteners, fluorescent whitening agents or other brightening or whitening agents known in the art can be incorporated in the instant compositions when they are designed for fabric treatment or laundering, at levels typically from about 0.05% to about 1.2%, by weight, of the detergent compositions herein. Commercial optical brighteners which may be useful in the present invention can be classified into subgroups, which include, but are not necessarily limited to, derivatives of stilbene, pyrazoline, coumarin, carboxylic acids, methinecyanines, dibenzothiophene-5,5-dioxide, azoles, 5- and 6-membered-ring heterocyclic brighteners, this list being illustrative and non-limiting. Examples of such brighteners are disclosed in "The Production and Application of Fluorescent Brightening Agents", M. Zahradnik, Published by John Wiley & Sons, New York (1982).

Specific examples of optical brighteners which are useful in the present compositions are those identified in U.S. Patent 4,790,856, issued to Wixon on December 13, 1988. These brighteners include the PHORWHITE series of brighteners from Verona. Other brighteners disclosed in this reference include: Tinopal UNPA, Tinopal CBS and Tinopal 5BM; available from Ciba-Geigy; Artic White CC and Artic White CWD, available from Hilton-Davis, located in Italy; the 2-(4-styryl-phenyl)-2H-naphthol[1,2-d]triazoles; 4,4'-bis- (1,2,3-triazol-2-yl)-stilbenes; 4,4'-bis(styryl)bisphenyls; and the aminocoumarins. Specific examples of these brighteners include 4-methyl-7-diethyl- amino coumarin; 1,2-bis(-benzimidazol-2-yl)ethylene; 2,5-bis(benzoxazol-2-yl)thiophene; 2-styryl-napth-[1,2-d]oxazole; and 2-(stilbene-4-yl)-2H-naphtho- [1,2-d]triazole. See also U.S. Patent 3,646,015, issued February 29, 1972, to Hamilton. Anionic brighteners are typically preferred herein.

If desired, compositions herein may additionally incorporate a catalyst or accelerator to further improve bleaching or soil removal. Any suitable bleach catalyst can be used. For detergent compositions used at a total level of from

about 1,000 to about 5,000 ppm in water, the composition will typically deliver a concentration of from about 0.1 ppm to about 700 ppm, more preferably from about 1 ppm to about 50 ppm, or less, of the catalyst species in the wash liquor.

Bleach catalysts may also be used herein. Typical bleach catalysts comprise a 5 transition-metal complex, for example one wherein the metal co-ordinating ligands are quite resistant to labilization and which does not deposit metal oxides or hydroxides to any appreciable extent under the typically alkaline conditions of washing. Such catalysts include manganese-based catalysts disclosed in U.S. 10 Pat. 5,246,621, U.S. 5,244,594; U.S. 5,194,416; U.S. 5,114,606; and EP Nos. 549,271 A1, 549,272 A1, 544,440 A2, and 544,490 A1; preferred examples of $Mn^{IV}_{2}(\mu-O)_{3}(TACN)_{2}-(PF_{6})_{2}$ these catalysts include $Mn^{III}_{2}(\mu-O)_{1}(\mu Mn^{IV}_{4}(\mu-O)_{6}(TACN)_{4}(CIO_{4})_{4}$, $Mn^{III}_{Mn^{IV}_{4}-(\mu-O)_{1}(\mu-O)_{1}}$ OAc)₂(TACN)₂(ClO₄)₂, OAc)₂-(TACN)₂-(ClO₄)₃, Mn^{IV}-(TACN)-(OCH₃)₃(PF₆), and mixtures thereof wherein TACN is trimethyl-1,4,7-triazacyclononane or an equivalent macrocycle; 15 though alternate metal-co-ordinating ligands as well as mononuclear complexes are also possible and monometallic as well as di- and polymetallic complexes and complexes of alternate metals such as iron or ruthenium are all within the present scope. Other metal-based bleach catalysts include those disclosed in 20 U.S. Pat. 4,430,243 and U.S. Pat. 5,114,611. The use of manganese with various complex ligands to enhance bleaching is also reported in the following United States Patents: 4,728,455; 5,284,944; 5,246,612; 5,256,779; 5,280,117; 5,274,147; 5,153,161; and 5,227,084.

Transition metals may be precomplexed or complexed *in-situ* with suitable donor ligands selected in function of the choice of metal, its oxidation state and the denticity of the ligands. Other complexes which may be included herein are those of U.S. Application Ser. No. 08/210,186, filed March 17, 1994.

The present invention will be further illustrated by the following examples.

Examples

The following compositions were prepared in accordance with the present invention. All amounts are described in weight % of the total composition.

0.5%

6.8%

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to balance

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Composition 1

	Dobanol 45-7	5%
	NaPS	1%
10	Benzoyl Lauroyl Peroxide	0.5%
	H2O2	6.8%
	Water and minors	to balance
	рН	4
15	Composition 2	
	Dobanol 45-7	5%
	NaPS	1%
	Isopar M	1.5%
20	Benzoyl Lauroyl Peroxide	2%
	Water and minors	to balance
	рН	4
25	Composition 3	
	Dobanol 45-7	3%
	NaPS	3%
	Isopar M	1.5%

Benzoyl Lauroyl Peroxide

Water and minors

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H2O2

ΡH

Composition 4

	Dobanoi 45-7	5%
5	NaPS	1%
	Isopar M	1.5%
	Benzoyl Lauroyl Peroxide	0.5%
	HEDP	0.16%
	H2O2	6.8%
10	Water and minors	to halance

10 Water and minors to balance

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Composition 5

15	Dobanol 45-7	5%
	NaPS	1%
	Isopar M	1.5%
	p-Pentyl-Benzoyl Lauroyl Peroxide	0.5%
	H2O2	6.8%
20	Water and minors	to balance
	pН	4

Composition 6

25	NaAS	2.7%
	Dobanol 23-3	2.5%
	Dobanol 91-10	2.6%
	Isopar M	1.5%
	Benzoyl Lauroyl Peroxide	0.5%
30	H2O2	6.8%
	Water and minors	to balance
	На	4



Composition 7

5	Dobanol 23-6.5	7.0%
	Dobanol 23-3	1.5%
	Dobanol 91-10	1.6%
	NaAS	1.7%
	Isopar M	1.5%
10	Benzoyl Lauroyl Peroxide	0.5%
	H2O2	6.8%
	Water and minors	to balance
	Нα	Λ

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